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The Fate of Bromoform in the Troposphere and Lower Stratosphere

by

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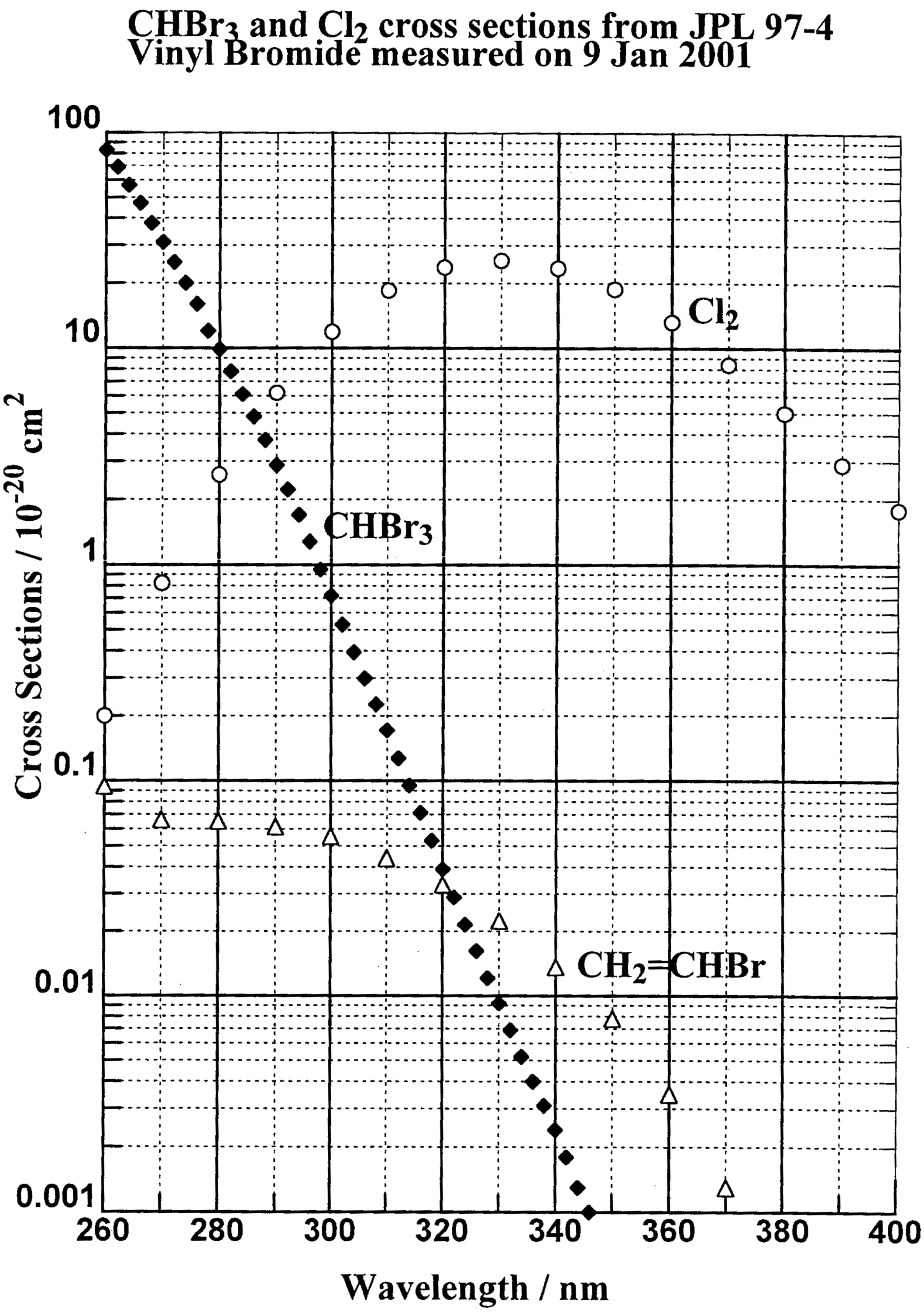
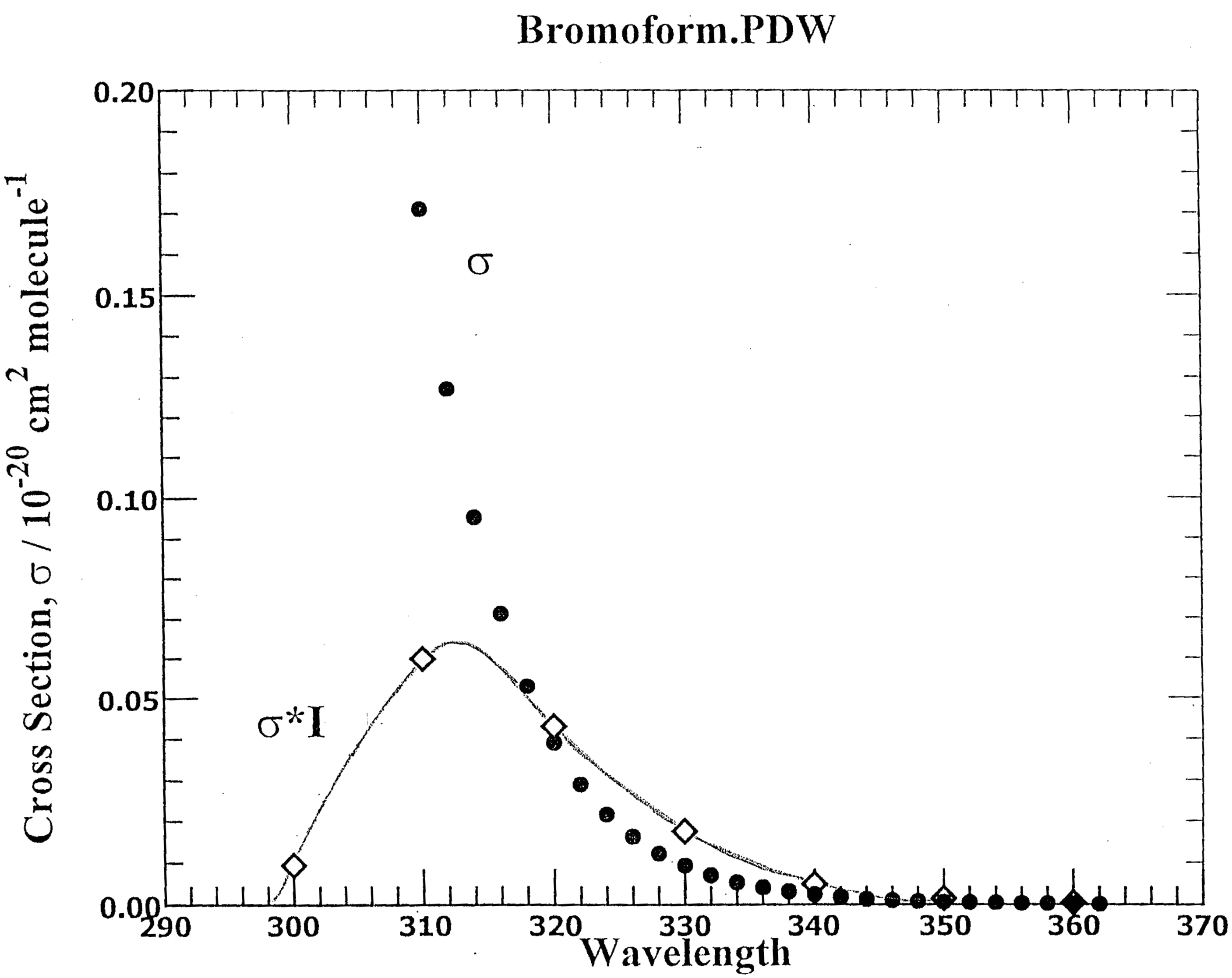
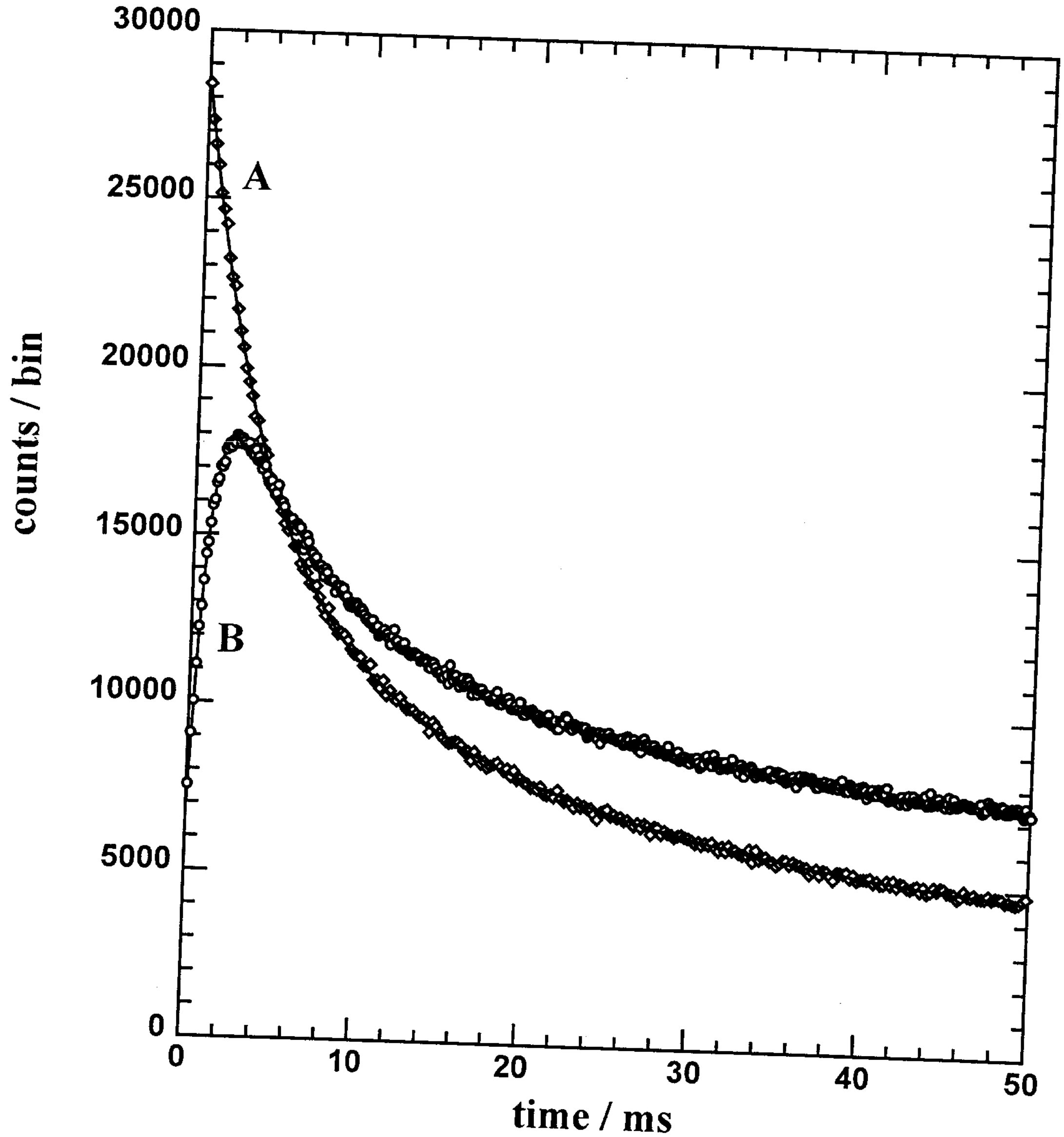

CHBr3 and Cl2 cross sections from JPL 97-4
Vinyl Bromide measured on 9 Jan 2001
100
10
1
0.1
0.01
0.001
Cross Sections / 10-20 cm2
Cl2
CHBr3
CH2=CHBr
260
280
300
320
340
360
380
400
Wavelength / nm



Bromoform.PDW
0.20
0.15
0.10
0.05
0.00
Cross Section, σ / 10^-20 cm^2 molecule^-1
σ
σ*I
290
300
310
320
330
340
350
360
370
Wavelength

Fig. 1



30000
25000
20000
15000
10000
5000
0
counts / bin
A
B
0
10
20
30
40
50
time / ms

Fig. 2

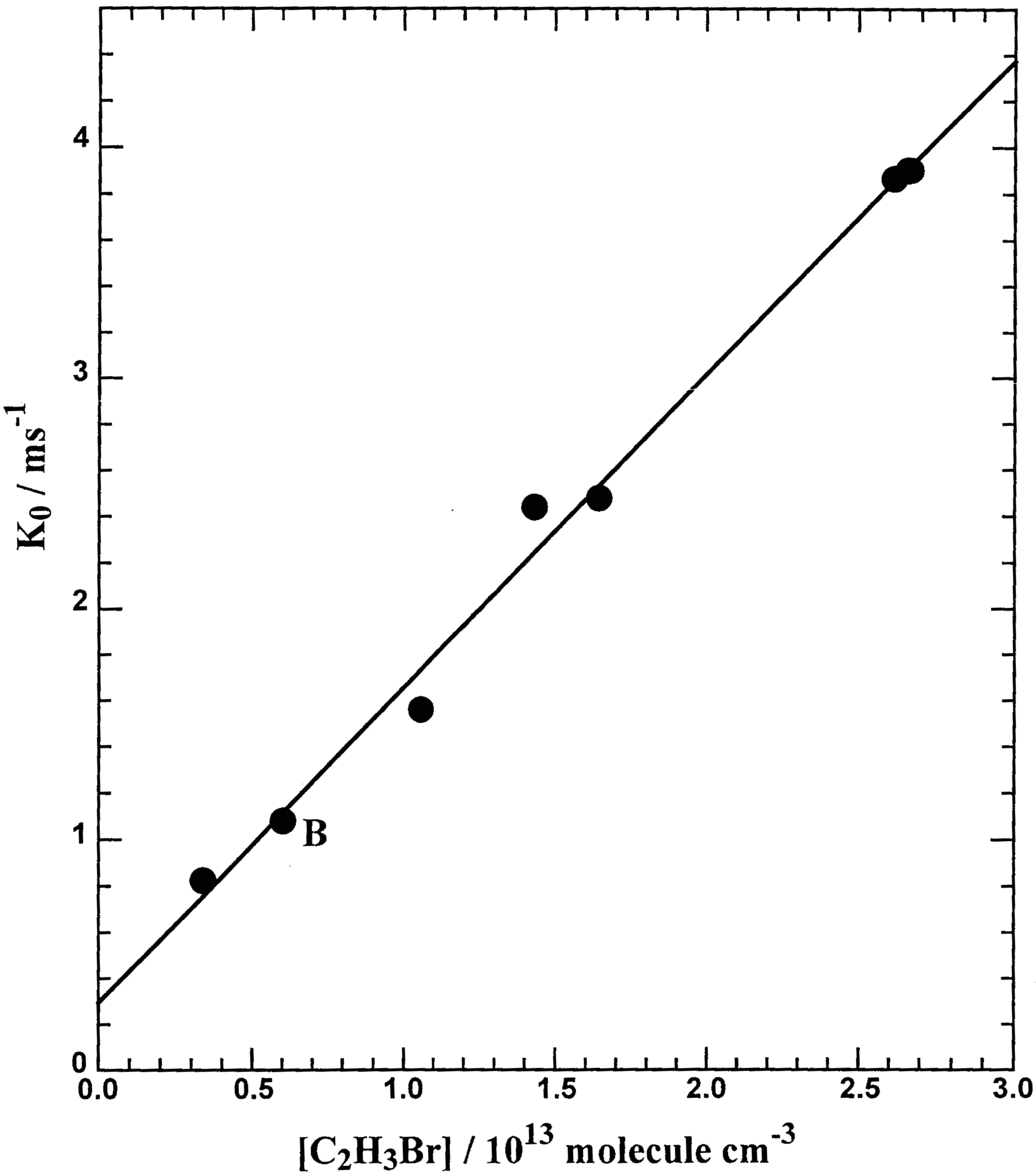
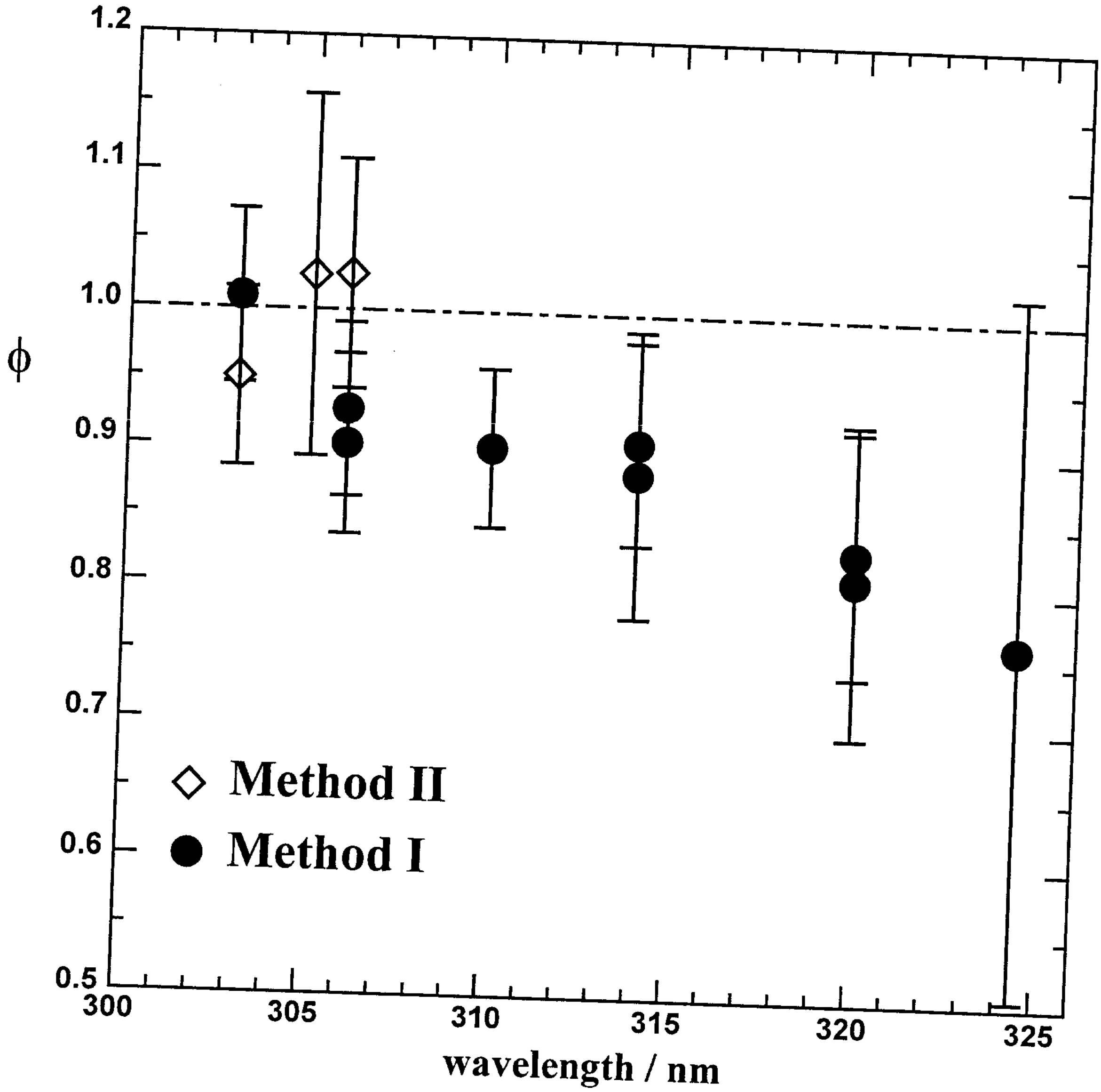


Fig. 3



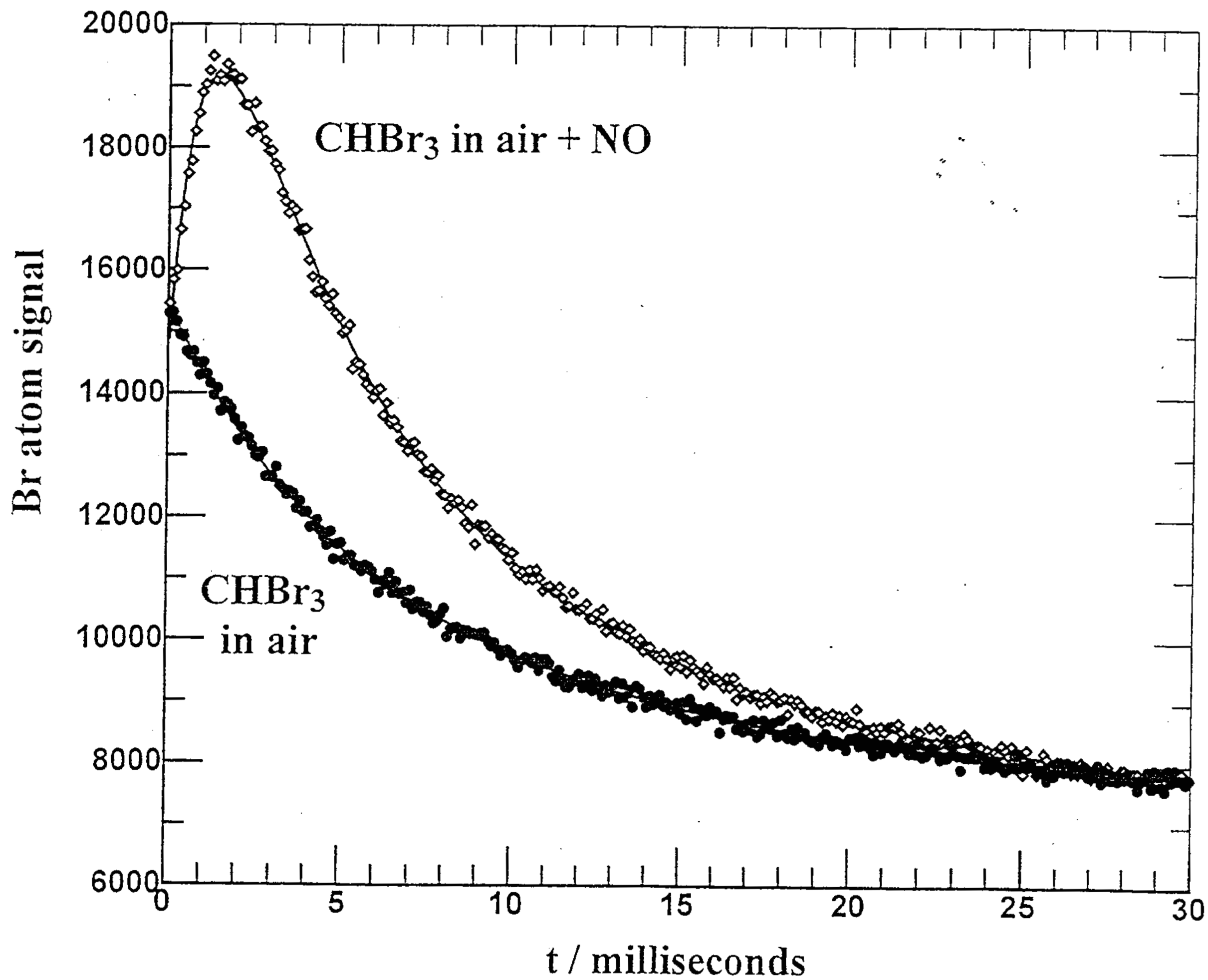
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
φ
300
305
310
315
320
325
wavelength / nm
Method II
Method I

$$CHBr_3 + h\nu \dashrightarrow Br + CHBr_2$$

$$CHBr_2 + O_2 \dashrightarrow OOCHBr_2$$

$$OOCHBr_2 + NO \dashrightarrow NO_2 + OCHBr_2$$

$$\left.\begin{array}{l} OCHBr_2 + O_2 \dashrightarrow HO_2 + OCBr_2 \\ OCHBr_2 \dashrightarrow Br + OCHBr \end{array}\right\} \quad ?$$



Assumed Mechanism

Initiation:

$CHBr_3 + h\nu \longrightarrow CHBr_2 + Br$

Assume immediately after the laser pulse, $[Br] = [CHBr_2] = S0$

Loss of $CHBr_2$:

$CHBr_2 + O_2 \xrightarrow{k1a} CHBr_2O_2$

$CHBr_2 + NO \xrightarrow{k1b} CHBr_2NO$

$CHBr_2 \xrightarrow{k1c}$ diffusional loss

let $CHBr_2 = R$, then solving,

$\mathbf{[R] = S0\ exp(-K1\ t)}$ where

$\mathbf{K1 = k1a[O_2] + k1b[NO] + k1c}$

Loss of $CHBr_2O_2$:

$CHBr_2O_2 + NO \xrightarrow{k2a} CHBr_2O + NO_2$

$CHBr_2O_2 \xrightarrow{k2c}$ diffusional loss

let $CHBr_2O_2 = RO_2$ and

$\mathbf{K2 = k2a[NO] + k2c}$, then

$$\mathbf{[RO_2] = k1a[O_2]S0\{ exp(-K2\ t) - exp(-K1\ t) \}/(K1 - K2)}$$

Formation and loss of Br:

Will assume that every $CHBr_2O$ that is formed rapidly decomposes to Br and CHBrO :

$CHBr_2O \xrightarrow{fast} CHBrO + Br$

$Br \xrightarrow{k3c}$ diffusional loss

$\mathbf{K3 = k3c}$ (only loss process)

$$d[Br]/dt = k2a[NO][RO2] - K3[Br]$$

Solving this differential equation using the previous expression for [RO2], and the boundary condition that [Br] = S0 at time = 0, yields:

$$\mathbf{[Br] = S0\ exp(-K3\ t) + K1\ K2\ F1\ F2\ S0 \{M2/(K2 - K3) - M1/(K1 - K3)\}/(K1 - K2)}$$

where $\mathbf{F1 = k1a[O2]/K1}$ = fraction of R that forms RO_2

$\mathbf{F2 = k2a[NO]/K2}$ = fraction of RO_2 that forms RO, and thus gives a second Br atom

$\mathbf{M1 = \{exp(-K3\ t) - exp(-K1\ t)\}}$

$\mathbf{M2 = \{exp(-K3\ t) - exp(-K2\ t)\}}$

For fitting the experimental data, three modifications were made to this theoretical expression:

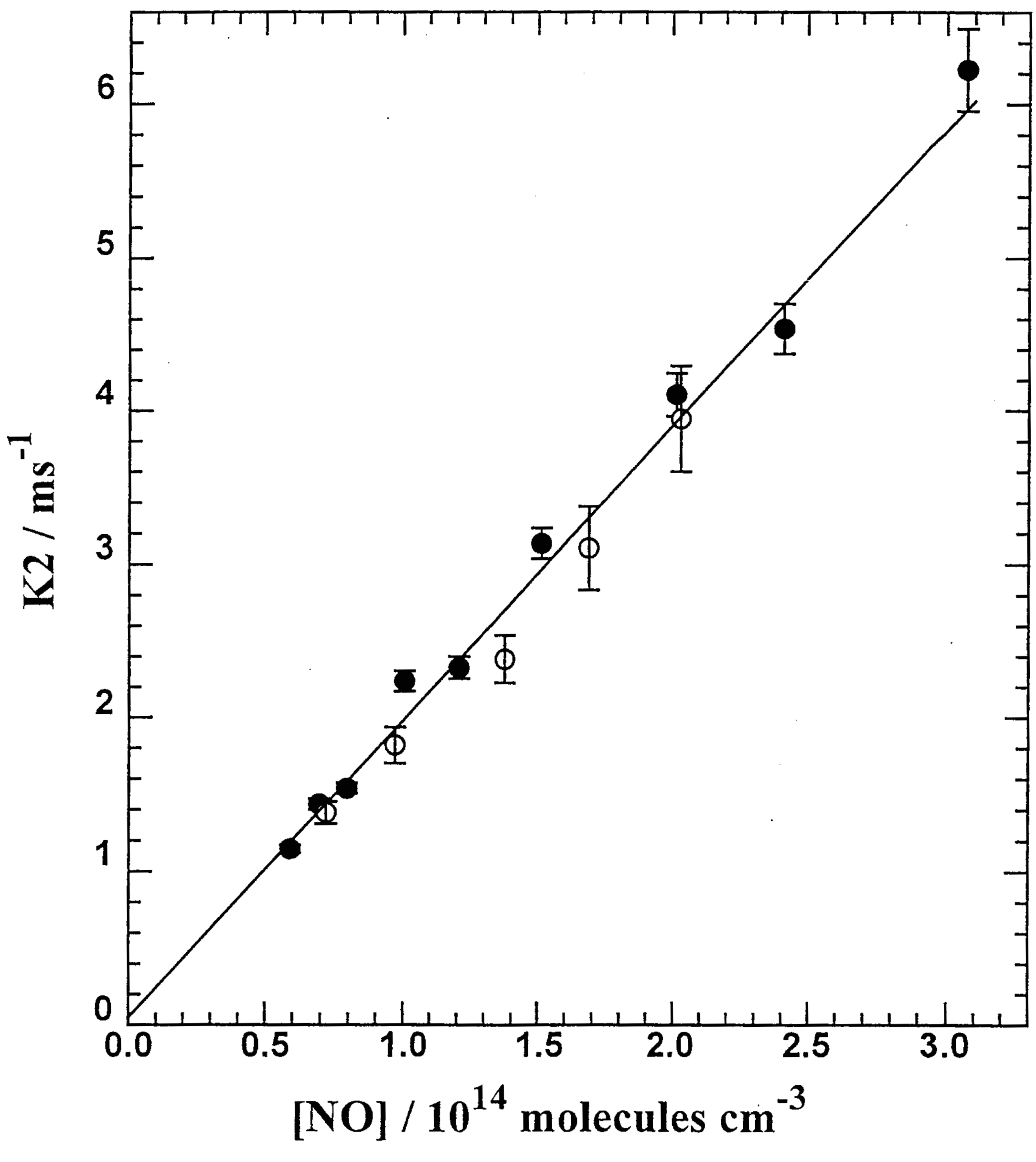
1. A constant, **Bk**, was added to account for the background count observed as t -->   ;
2. A fitted constant, **S1**, is used in place of the term (F1 F2 S0) so that the assumption that every RO decomposes to give a Br atom can be tested by comparing S1/(F1 F2) with S0;
3. At long times the Br signal displays a double exponential decay, whether NO is present or not; so an additional term was added of the form S2 M3, where **S2** is a fitted constant, typically 45% as large as (S0 + S1), and **M3 = {exp(-K4 t) – exp(-K3 t)}** .

The resulting equation used in the weighted least squares fits was:

$$\mathbf{Signal = S0\ exp(-K3\ t) + K1\ K2\ S1\ \{M2/(K2-K3) - M1/(K1-K3)\}/(K1-K2) + S2\ M3 + Bk}$$

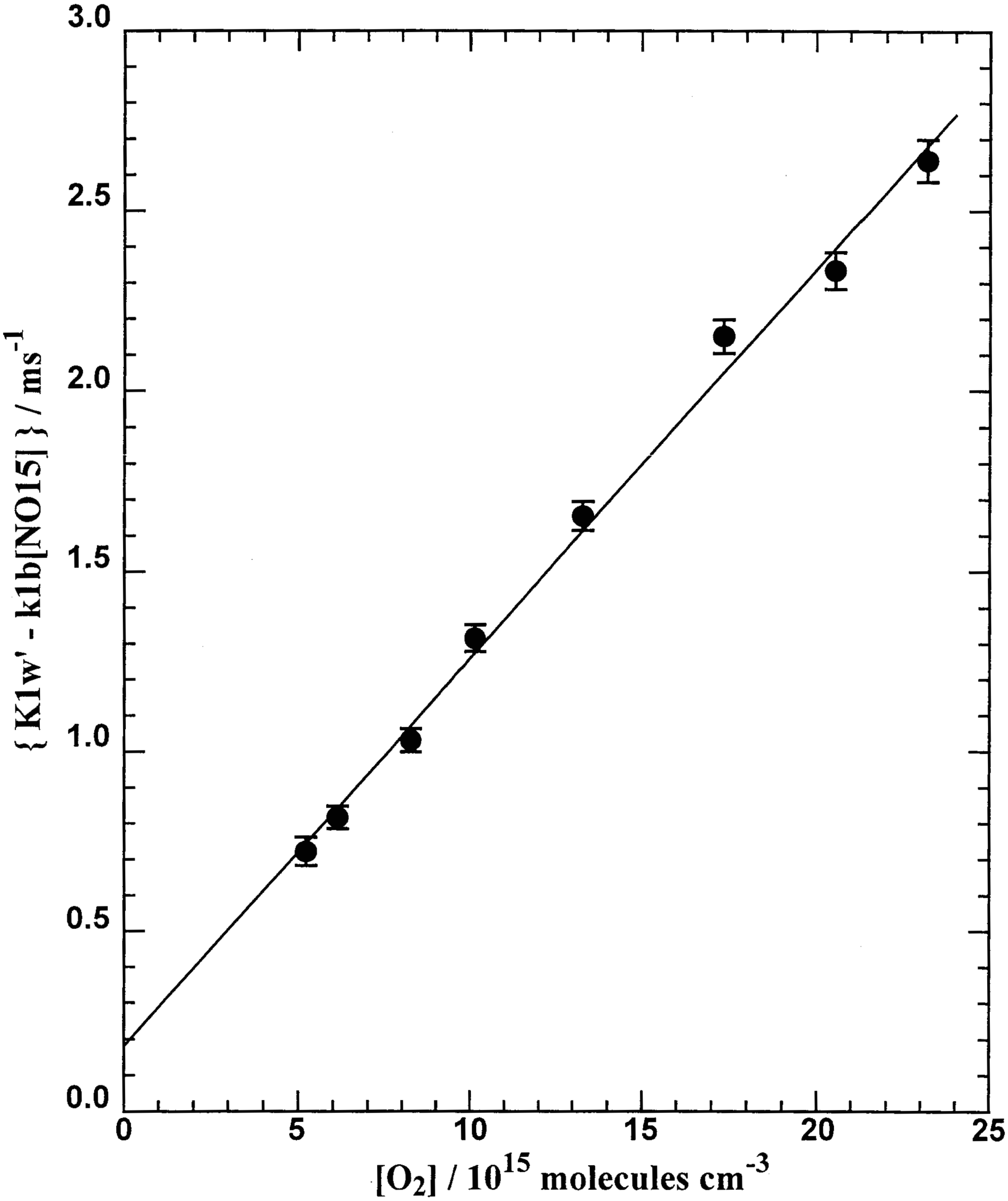
Rise time constant K2 vs. [NO]

$CHBr_3$/air/NO at 10 Torr total pressure
266 nm (17 and 19 June 2002)
303 nm (8 May 2002)



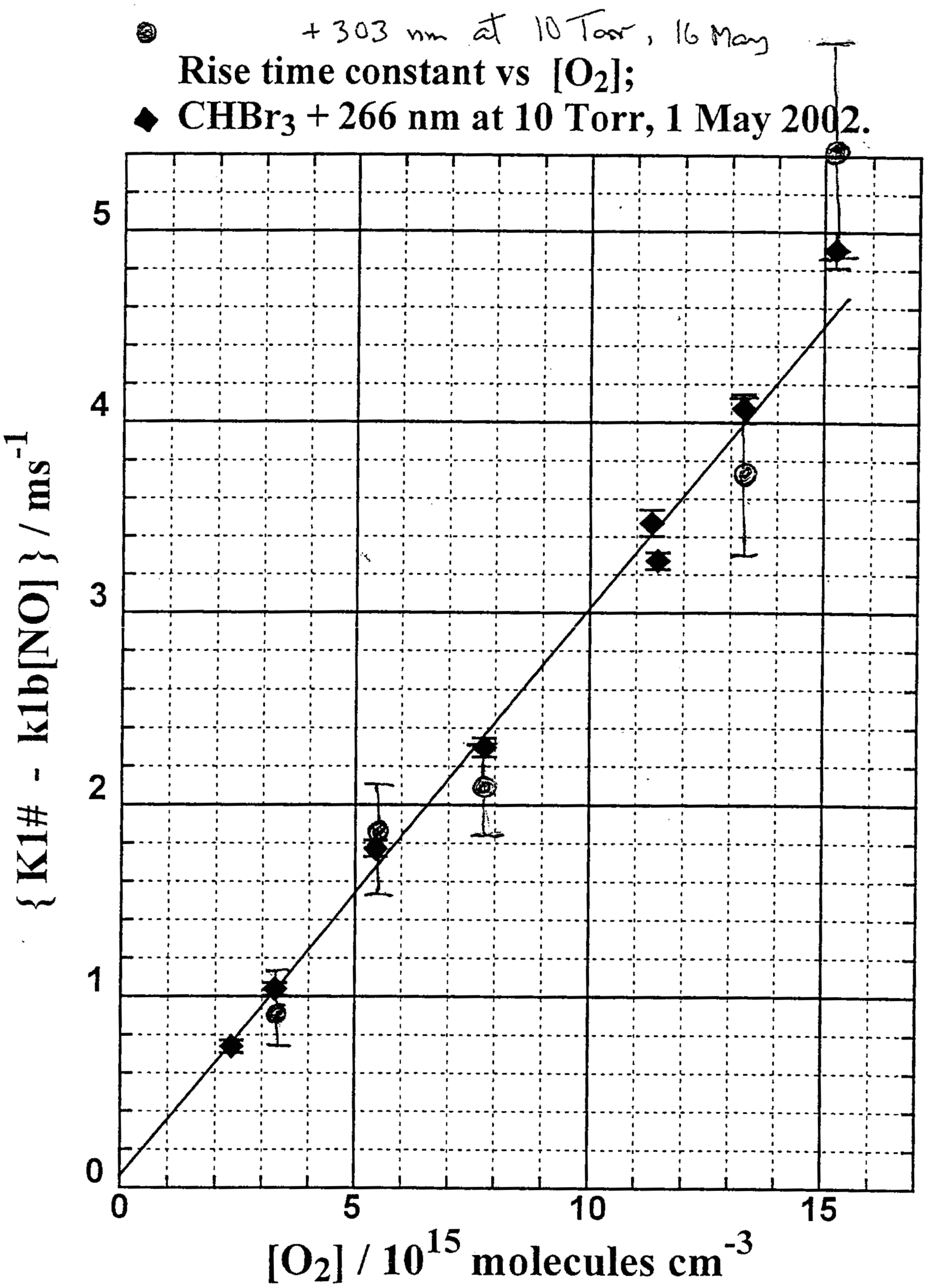
k2a = (1.93 +/- 0.04) 10^{-11} cm^3 $molecule^{-1}$ s^{-1}

Time constant K1 vs. $[O_2]$
$CHBr_3/O_2/NO$ at 2 Torr total pressure
266 nm (22 May 2002)



Slope = k1a = $1.07_8 \times 10^{-13}$ cm^3 molecules^{-1} s^{-1}

using k1b = $5.8_7 \times 10^{-13}$ and imposing intercept = k1c = 0.18 ms^{-1}



Slope = k1a = (2.96 +/- 0.57) 10^{-13} cm^3 $molecule^{-1}$ s^{-1}

Intercept = k1c = 0.062 ms^{-1}

Use k1b = 1.06 10^{-12} cm^3 $molecule^{-1}$ s^{-1}

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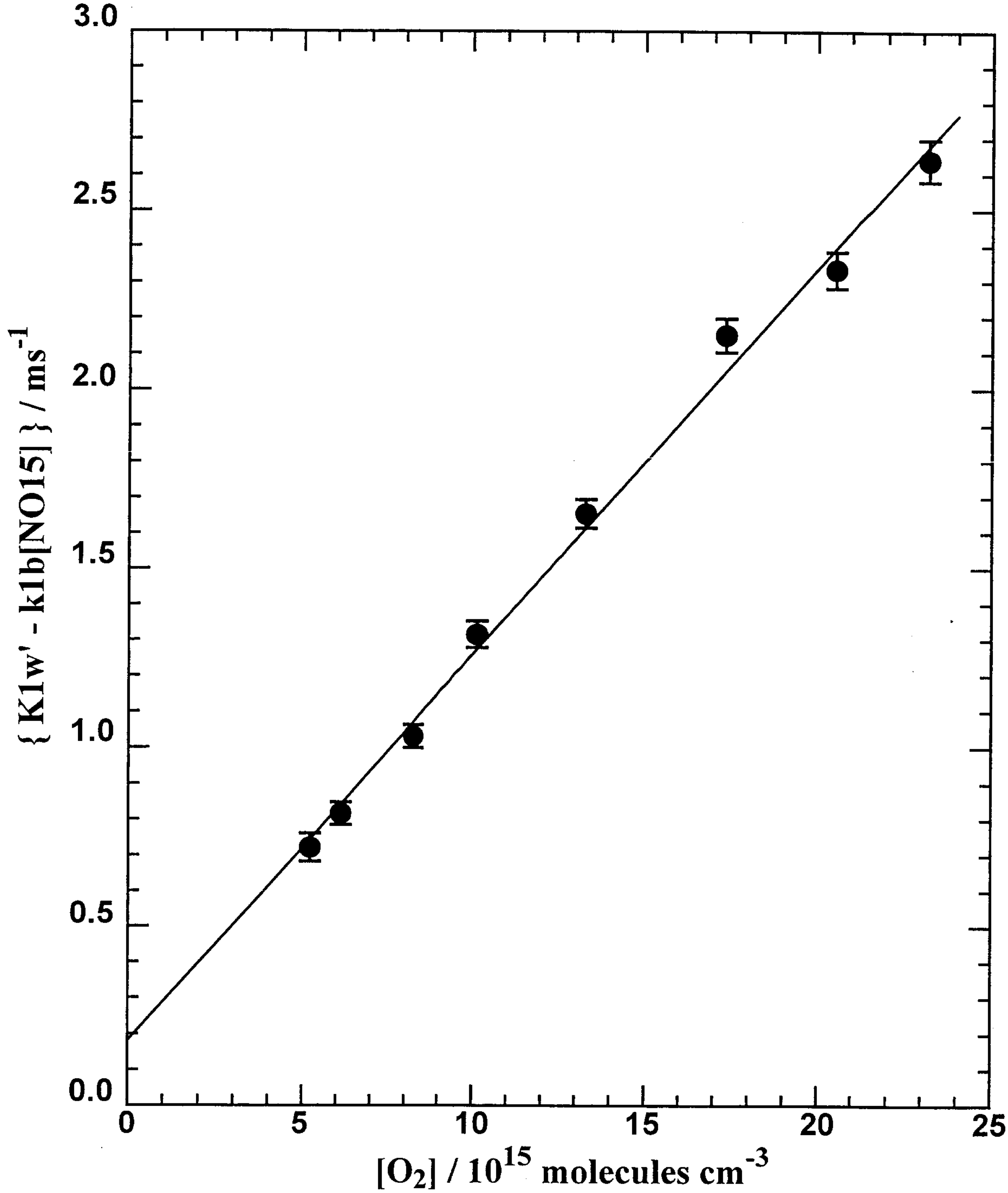
Time constant K1 vs. [O_2]
$CHBr_3/O_2/NO$ at 2 Torr total pressure
266 nm (22 May 2002)



Slope = k1a = $1.07_8 \times 10^{-13}$ cm^3 molecules^{-1} s^{-1}

using k1b = $5.8_7 \times 10^{-13}$ and imposing intercept = k1c = 0.18 ms^{-1}

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P / Torr	k1a / 10^{-13}	k1b / 10^{-13}	k2a / 10^{-11}	S1 / (S0 F1 F2)
10	2.96	~10.6	1.93	1.00 +/- 0.015 (266 nm) 0.97 +/- 0.12 (303 nm)
2	1.08	~5.9	~2.0	0.95 +/- 0.06 (266 nm)